Table 2. *Crystal data for the three new stacking variants*

Layer type	Space group	Stacking order	Lattice constants (Å)† Mg–Zn–Cu	Mg–Zn–Ag
8-layer	$P6_3/mmc$	$AB'AB'A'CA'C$	$a = 5{\cdot}21$	$a = 5{\cdot}21$
			$c = 34{\cdot}2$	$c = 34{\cdot}4$
9-layer	$R\bar{3}m$	$AB'ABC'BCA'C$	$a = 5{\cdot}19$	$a = 5{\cdot}21$
			$c = 38{\cdot}4$	$c = 38{\cdot}7$
10-layer	$P6_3/mmc$	$ABC'BCA'C'BC'B'$	$a = 5{\cdot}17$	$a = 5{\cdot}22$
			$c = 42{\cdot}5$	$c = 43{\cdot}0$

† All the lattice constants are given for a hexagonal unit cell.

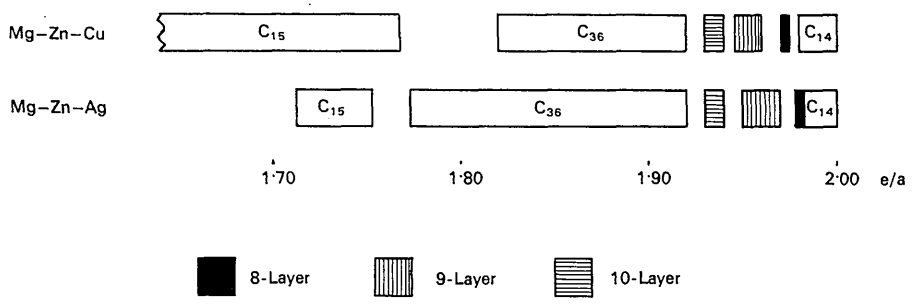

Fig. 2. Structural changes in the Mg–Zn–Cu and Mg–Zn–Ag alloys as a function of the electron-atom ratio.

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Remeasurements of the Structure of Potassium-2,2,5,5-tetramethyl-3-carboxypyrroline-1-oxyl

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The structure of the nitroxide free radical, $C_9H_{13}NO_3K.\frac{1}{3}H_2O$ has been redetermined using data obtained for the full copper sphere with an automatic single-crystal diffractometer and Mo $K\alpha$ X-radiation. There are two independent molecules of the radical per asymmetric unit and after refinement to $R = 0{\cdot}07$ these were found to be identical and planar within experimental error. The irregularities observed in a previous investigation, particularly an abnormally short C–C bond which occurred in both crystallographically independent molecules in the asymmetric unit, did not recur and the expected molecular symmetry was observed.

Introduction

A crystal of the potassium salt of 2,2,5,5-tetramethyl-3-carboxypyrroline-1-oxyl was used previously (Kruger & Boeyens, 1968) to determine the geometry of a sterically protected nitroxide radical incorporated in a five-membered ring. This system is important as a spin label (Hamilton & McConnell, 1968) and accurate structure parameters are desirable.

Because of insufficient data certain irregularities were observed, particularly for bonds lying parallel to [010]. The fact that one particular bond was similarly

Table 1. *Fractional coordinates and anisotropic thermal parameters with their standard deviations*

$$T=\exp\left[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\right].$$

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K	0	0·6763 (3)	0·9537 (2)	0·0017 (1)	0·0102 (4)	0·0061 (2)	0	0	−0·0008 (3)
C(1)	0	0·0197 (15)	0·5981 (9)	0·0024 (3)	0·0121 (20)	0·0035 (7)	0	0	−0·0009 (10)
C(2)	0	0·1943 (14)	0·6711 (9)	0·0016 (2)	0·0126 (19)	0·0041 (7)	0	0	−0·0027 (10)
C(3)	0	0·3522 (16)	0·6123 (10)	0·0033 (3)	0·0128 (21)	0·0047 (8)	0	0	−0·0006 (11)
C(4)	0	0·3210 (17)	0·4840 (11)	0·0035 (4)	0·0171 (23)	0·0053 (10)	0	0	−0·0013 (13)
C(5)	0	0·1901 (16)	0·7967 (9)	0·0016 (2)	0·0151 (22)	0·0047 (7)	0	0	0·0006 (11)
C(6)	0·0622 (7)	0·3884 (17)	0·4259 (9)	0·0062 (5)	0·0312 (29)	0·0075 (8)	−0·0051 (10)	0·0041 (5)	−0·0023 (12)
C(8)	0·0611 (5)	0·8998 (13)	0·6119 (9)	0·0032 (3)	0·0199 (20)	0·0082 (8)	0·0034 (6)	−0·0006 (4)	−0·0026 (11)
O(1)	0	0·0163 (17)	0·3923 (9)	0·0052 (4)	0·0271 (28)	0·0064 (8)	0	0	−0·0049 (13)
O(2)	0	0·0311 (11)	0·8436 (7)	0·0024 (2)	0·0124 (14)	0·0048 (5)	0	0	0·0013 (8)
O(3)	0	0·3411 (11)	0·8501 (7)	0·0028 (2)	0·0136 (15)	0·0052 (6)	0	0	−0·0028 (8)
N	0	0·1086 (14)	0·4837 (9)	0·0031 (3)	0·0183 (20)	0·0051 (8)	0	0	−0·0023 (10)
K′	0·0927 (7)	0·1708 (2)	0	0·0018 (1)	0·0108 (2)	0·0064 (1)	−0·0001 (1)	−0·0003 (1)	0·0002 (2)
C(1′)	0·2150 (4)	0·8478 (11)	0·2270 (7)	0·0019 (2)	0·0139 (15)	0·0063 (6)	0·0005 (4)	−0·0011 (3)	−0·0021 (9)
C(2′)	0·1814 (3)	0·6668 (10)	0·1873 (6)	0·0016 (1)	0·0109 (12)	0·0044 (4)	−0·0008 (4)	−0·0007 (2)	−0·0006 (7)
C(3′)	0·2067 (4)	0·5158 (11)	0·2318 (8)	0·0024 (2)	0·0109 (15)	0·0090 (8)	−0·0001 (5)	−0·0015 (4)	0·0004 (9)
C(4′)	0·2644 (5)	0·5507 (12)	0·3073 (10)	0·0031 (3)	0·0132 (15)	0·0118 (10)	−0·0009 (6)	−0·0030 (5)	0·0024 (11)
C(5′)	0·1258 (4)	0·6684 (10)	0·1083 (6)	0·0018 (2)	0·0129 (13)	0·0049 (5)	0·0002 (4)	−0·0008 (2)	−0·0004 (8)
C(6′)	0·3277 (5)	0·4719 (16)	0·2048 (13)	0·0027 (3)	0·0268 (26)	0·0174 (15)	0·0030 (8)	−0·0018 (6)	−0·0041 (17)
C(7′)	0·2464 (7)	0·5067 (19)	0·4351 (10)	0·0059 (5)	0·0358 (30)	0·0078 (9)	−0·0053 (10)	−0·0028 (6)	0·0085 (15)
C(8′)	0·2485 (5)	0·9588 (12)	0·1294 (8)	0·0030 (2)	0·0187 (19)	0·0076 (7)	−0·0031 (6)	−0·0010 (4)	0·0032 (10)
C(9′)	0·1708 (5)	0·9743 (12)	0·3011 (10)	0·0026 (3)	0·0172 (18)	0·0105 (10)	0·0016 (6)	−0·0007 (4)	−0·0048 (11)
C(1′)	0·3073 (3)	0·8629 (9)	0·3538 (7)	0·0031 (2)	0·0232 (15)	0·0114 (7)	−0·0009 (5)	−0·0035 (3)	−0·0015 (9)
O(2′)	0·1058 (3)	0·8254 (8)	0·0718 (6)	0·0031 (2)	0·0134 (11)	0·0107 (6)	−0·0007 (4)	−0·0028 (3)	0·0023 (8)
O(3′)	0·1022 (3)	0·5119 (8)	0·0820 (6)	0·0029 (2)	0·0114 (10)	0·0097 (6)	−0·0002 (4)	−0·0020 (3)	−0·0031 (7)
N′	0·2665 (3)	0·7612 (9)	0·3002 (7)	0·0023 (2)	0·0167 (13)	0·0068 (6)	−0·0001 (4)	−0·0017 (3)	−0·0012 (7)
O(H_2O)	0	0·1068 (29)	0·1682 (10)	0·0038 (4)	0·0925 (17)	0·0068 (9)	0	0	−0·0010 (23)

affected in the two independent molecules in the asymmetric unit decisively necessitated a remeasurement of the structure.

Experimental

The same cylindrical crystal with an average diameter of 0·5 mm described before (Kruger & Boeyens, 1968) was used in this study. It has the space group $Pmn2_1$, No. 31 in *International Tables for X-ray Crystallography* (1965), and the cell dimensions as refined on a Hilger & Watts four-circle diffractometer are: $a=20{\cdot}666\pm 0{\cdot}010$, $b=7{\cdot}064\pm 0{\cdot}004$ and $c=11{\cdot}826\pm 0{\cdot}006$ Å.

All the intensities within the copper sphere were measured on a diffractometer using an ω-scan with a set of balanced filters. Observations at the positions of systematically absent reflexions established a minimum meaningful reading of 100 counts. According to this criterion the intensities of 2176 reflexions were recorded and for 524 reflexions the intensities were below the detection limit.

A uniform value of 50 (counts) was assigned to all the unobserved reflexions and the usual corrections were applied to all intensities. The low $\mu R=0{\cdot}14$ obviated corrections for absorption.

The best coordinates of Kruger & Boeyens (1968) were used to start an anisotropic full-matrix refinement using the program *ORFLS* of Busing, Martin & Levy (1962) on an IBM 360/65 computer. Refinement

Table 2. *Observed and calculated structure factors on an absolute scale*

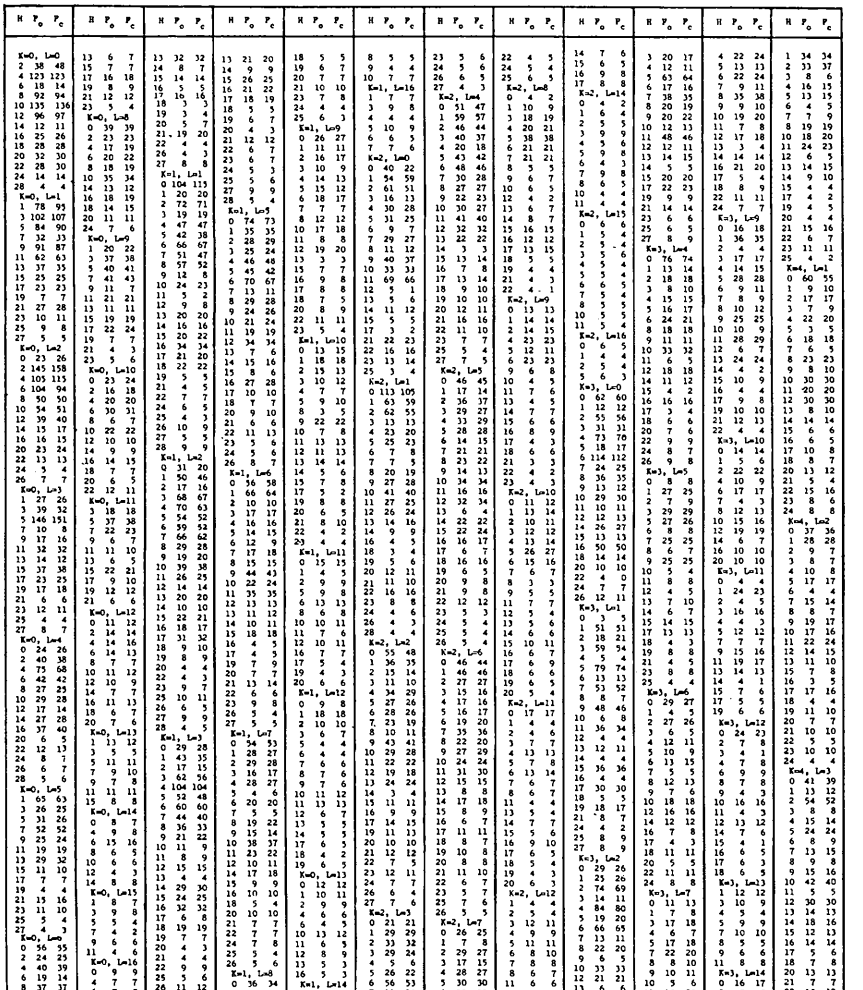
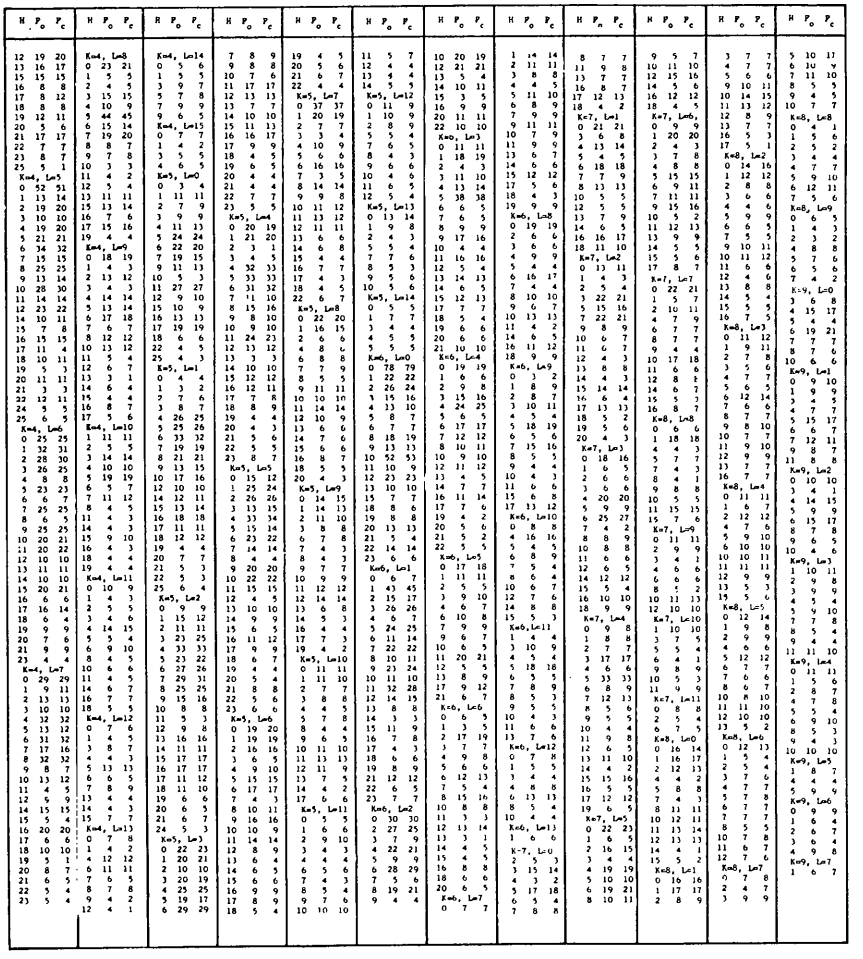


Table 2 (*cont.*)



was considered complete when the parameter shifts were all less than 10% of the estimated standard deviations. The discrepancy, defined as $R = \sum ||F_c| - F_o| / \sum F_o$, was equal to 0·08 at this stage. An inspection of the calculated structure factors revealed that although they were all uniformly low, there was considerable scatter in the correspondence between observed and calculated structure factors of the individual unobserved reflexions. These were therefore excluded from the final refinement as suggested by Dunning & Vand (1969) and R was 0·07 for the observed reflexions alone.

Results

The final atomic and anisotropic temperature parameters are listed in Table 1. The observed and calculated structure factors are given in Table 2. The packing is as described before (Kruger & Boeyens, 1968) and only the new molecular parameters will be considered here.

One of the molecules in the asymmetric unit lies in a mirror plane with all its atoms, with the exception of the methyl groups. The other independent molecule is also flat and the equation of the normal to the molecular plane is given by

$$-0{\cdot}6151\ xa + 0{\cdot}0627\ yb + 0{\cdot}7859\ zc = -0{\cdot}2565\ .$$

The deviations of individual atoms from this plane are given in Table 3. These deviations are not significant except for the potassium ion which does not lie in the molecular plane.

Table 3. *Deviations from planarity of the pyrroline ring in the general position and the distances of the associated atoms from this plane*

C(1′)	0·009 Å	K′	−0·846 Å
C(2′)	−0·013	C(5′)	−0·040
C(3′)	0·011	O(1′)	0·021
C(4′)	−0·004	O(2′)	−0·056
N′	−0·003	O(3′)	−0·054

The molecular parameters of the two independent molecules are summarized in Table 4 and the molecular geometry averaged over chemically equivalent bonds is shown in Fig. 1. It appears that the irregularities observed before (Kruger & Boeyens, 1968) were due to weak scaling of the scant photographic

data. The length of the nitroxide N–O bond is now also closer to the value of 1·26 Å found by Lajzérowicz-Bonneteau (1968) in a similar compound.

Table 4. *Observed molecular bond lengths and angles*

	Molecule	
Bond	Mirror plane	General position
C(1)–C(2)	1·504 ± 0·014 Å	1·529 ± 0·009 Å
C(2)–C(3)	1·315 ± 0·015	1·299 ± 0·010
C(3)–C(4)	1·533 ± 0·016	1·510 ± 0·012
C(4)–N	1·501 ± 0·015	1·490 ± 0·010
N—C(1)	1·492 ± 0·015	1·502 ± 0·010
N—O(1)	1·263 ± 0·013	1·277 ± 0·008
C(2)–C(5)	1·486 ± 0·014	1·481 ± 0·009
C(5)–O(2)	1·253 ± 0·013	1·260 ± 0·009
C(5)–O(3)	1·239 ± 0·013	1·248 ± 0·009
O(3)–K	2·666 ± 0·008	2·605 ± 0·006
C(1)–C(8)	1·529 ± 0·011	1·558 ± 0·012
C(1)–C(9)		1·549 ± 0·012
C(4)–C(6)	1·534 ± 0·012	1·509 ± 0·015
C(4)–C(7)		1·587 ± 0·015
H_2O–N	2·726 ± 0·016	
H_2O–K		2·798 ± 0·009
Angle		
C(1)–C(2)–C(3)	113·1 ± 0·9°	112·3 ± 0·6°
C(2)–C(3)–C(4)	113·6 ± 1·0	115·1 ± 0·7
C(3)–C(4)–N	98·4 ± 1·0	98·8 ± 0·7
C(4)–N—C(1)	114·8 ± 0·9	114·7 ± 0·7
N—C(1)–C(2)	100·1 ± 0·9	99·1 ± 0·6
C(1)–N—O(1)	124·0 ± 0·9	121·7 ± 0·6
C(4)–N—O(1)	121·2 ± 1·1	123·6 ± 0·7
C(1)–C(2)–C(5)	123·8 ± 1·0	122·7 ± 0·6
C(2)–C(5)–O(2)	117·4 ± 1·0	118·5 ± 0·6
C(2)–C(5)–O(3)	119·5 ± 1·0	117·0 ± 0·7
C(5)–O(3)–K	176·7 ± 0·8	160·4 ± 0·6
C(6)–C(4)–C(7)	114·0 ± 1·3	116·6 ± 1·0
N—C(4)–C(6)	108·0 ± 0·7	108·9 ± 0·9
N—C(4)–C(7)		104·8 ± 0·9
C(8)–C(1)–C(9)	111·3 ± 1·0	113·0 ± 0·7
N—C(1)–C(8)	109·3 ± 0·6	108·6 ± 0·7
N—C(1)–C(9)		109·1 ± 0·7
C(2)–C(1)–C(8)	113·1 ± 0·6	113·3 ± 0·7
C(2)–C(1)–C(9)		112·8 ± 0·6
C(3)–C(4)–C(6)	113·5 ± 0·7	115·3 ± 1·0
C(3)–C(4)–C(7)		110·3 ± 0·9

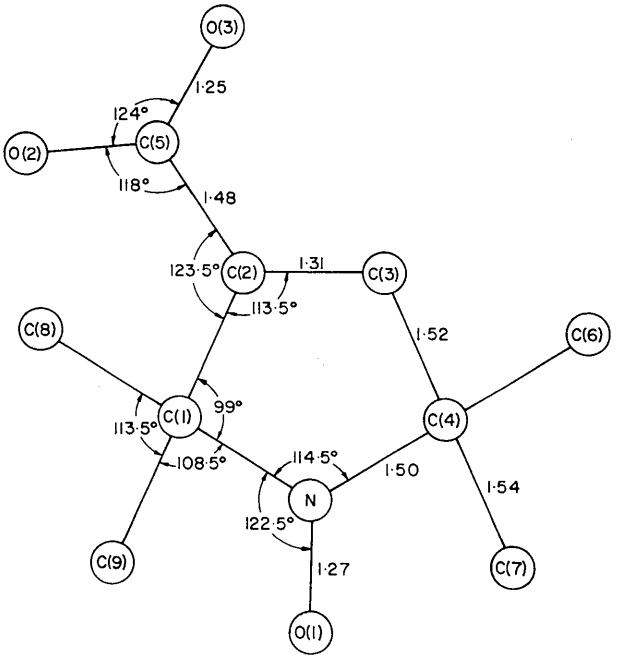


Fig. 1. Geometry of the organic anion averaged over chemically equivalent bonds and angles and assuming *mm* symmetry for the nitroxide ring.

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